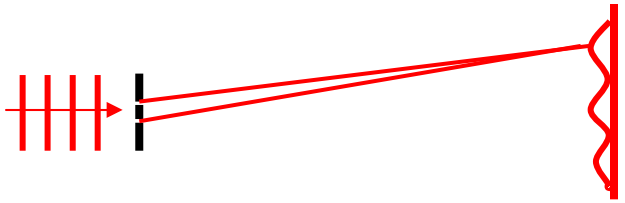
Coherent X-ray Scattering and X-ray Photon Correlation Spectroscopy

Laurence Lurio
Department of Physics
Northern Illinois University

What is Coherence?

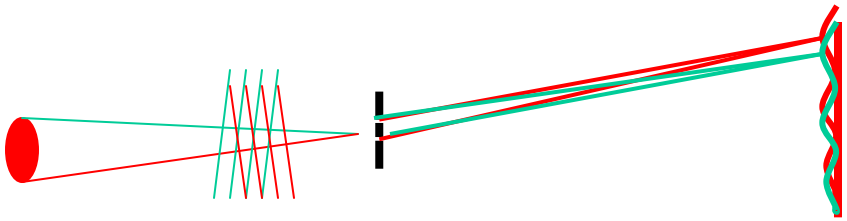
Ideal Young's double slit experiment



Intensity varies as

$$I = 2I_0\left[1+\cos\left(2\pi d\sin(\theta)/\lambda\right)\right]$$

Real Young's double slit experiment



Intensity varies as

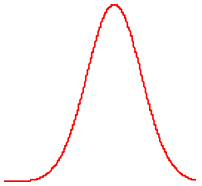
$$I = 2I_0\left[1+\beta\cos\left(2\pi d\sin(\theta)/\lambda\right)\right]$$

β is the contrast, determined by the angular size of the source

Coherence Length and Contrast

It is generally convenient to assume the source has a Gaussian intensity profile

$$I(x) = \frac{I_0}{\sqrt{2\pi}\xi} \exp\left[-\left(x - x_0\right)^2 / 2\sigma^2\right]$$

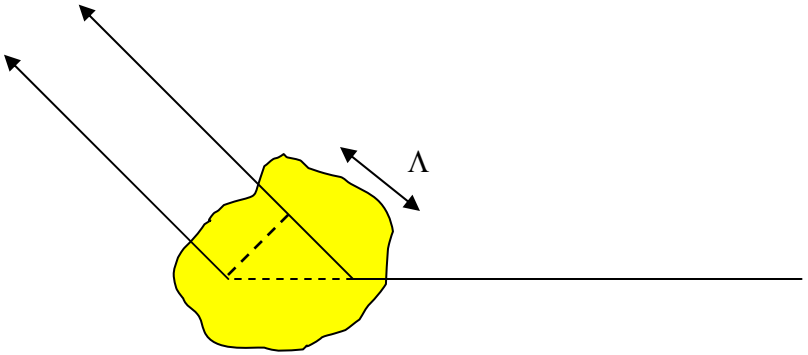


One can then define a coherence length

$$\xi = \frac{\lambda R}{2\sigma\sqrt{\pi}}$$

This characterizes the distance over which two slits would produce an interference pattern, or more generally the length scale over which any sample will produce interference effects.

Longitudinal coherence



$$\Lambda \approx \lambda(E / \Delta E)$$

e.g. the number of wavelengths that can be added before the uncertainty adds up to a full wavelength.

How Practical is it to Make X-rays Coherent?

Consider a point 65 meters downstream of an APS Undulator A

$$\lambda = 0.2\text{nm}, \quad \Delta\lambda/\lambda = 3\times10^{-4}$$

Ge 111

$$\sigma_x = 254\mu\text{m}, \sigma_y = 12\mu\text{m}$$

$$\xi_x = \frac{\lambda R}{2\sigma_x\sqrt{\pi}} = 14\mu\text{m}$$

$$\xi_y = \frac{\lambda R}{2\sigma y\sqrt{\pi}} = 306\mu\text{m}$$

$$\Lambda = 0.66\mu\text{m}$$

$$\sim 3\times10^{10}\,\text{Photons/Coherence Area}$$

Scattering of Coherent X-rays

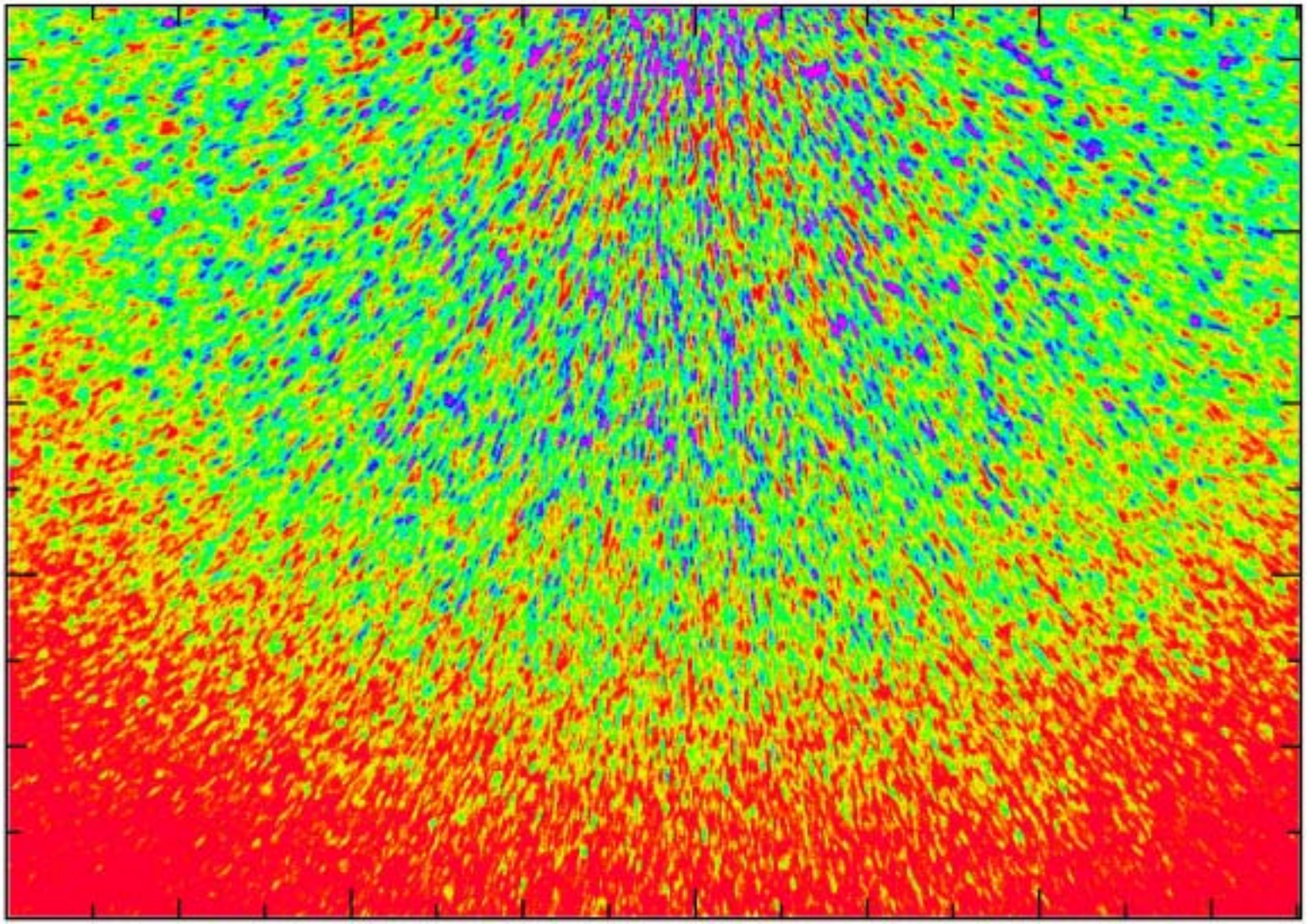
$$I(Q) \propto \int\int e^{i\vec{Q}\cdot\vec{r''}} \rho_e\left(\vec{r}\right)\rho_e\left(\vec{r}-\vec{r''}\right)d\vec{r}d\vec{r''}$$

For incoherent x-rays the actual scattering represents a statistical average over many incoherent regions within the sample and one obtains:

$$\rho_e\left(\vec{r}\right)\rho_e\left(\vec{r}-\vec{r''}\right) \approx \left\langle \rho_e\left(\vec{r}\right)\rho_e\left(\vec{r}-\vec{r''}\right)\right\rangle \equiv g\left(\vec{r}\right)$$

For coherent x-rays one measures the Fourier transform of the exact density distribution, not the average. What one observes is a speckle pattern superposed on the average scattering pattern.

Coherent Scattering from a Silica Aerogel



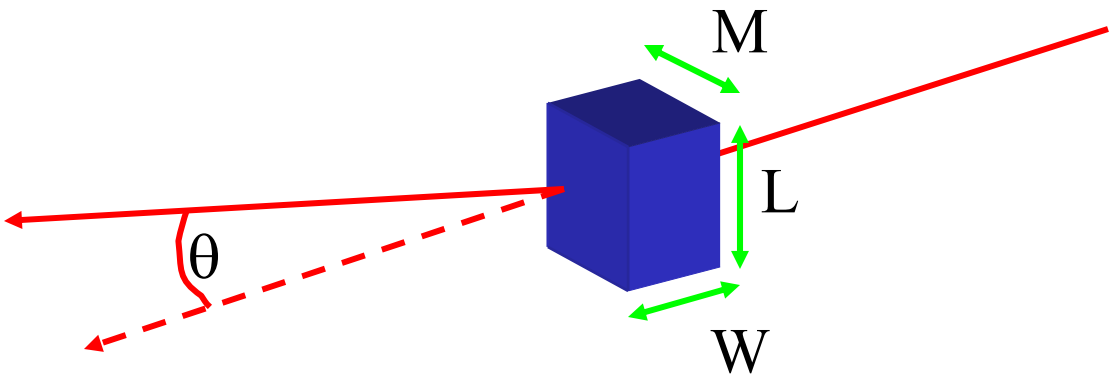
Speckle Size and Contrast

The average angular size of the speckles is, approximately, given by the diffraction limit of the illuminated sample area:

$$\Delta\theta \approx \lambda / L$$

The contrast is given by the ratio of the scattering volume

$V_s \approx MLW\sin(\theta)$ to the coherence volume $\Lambda\xi_x\xi_y$

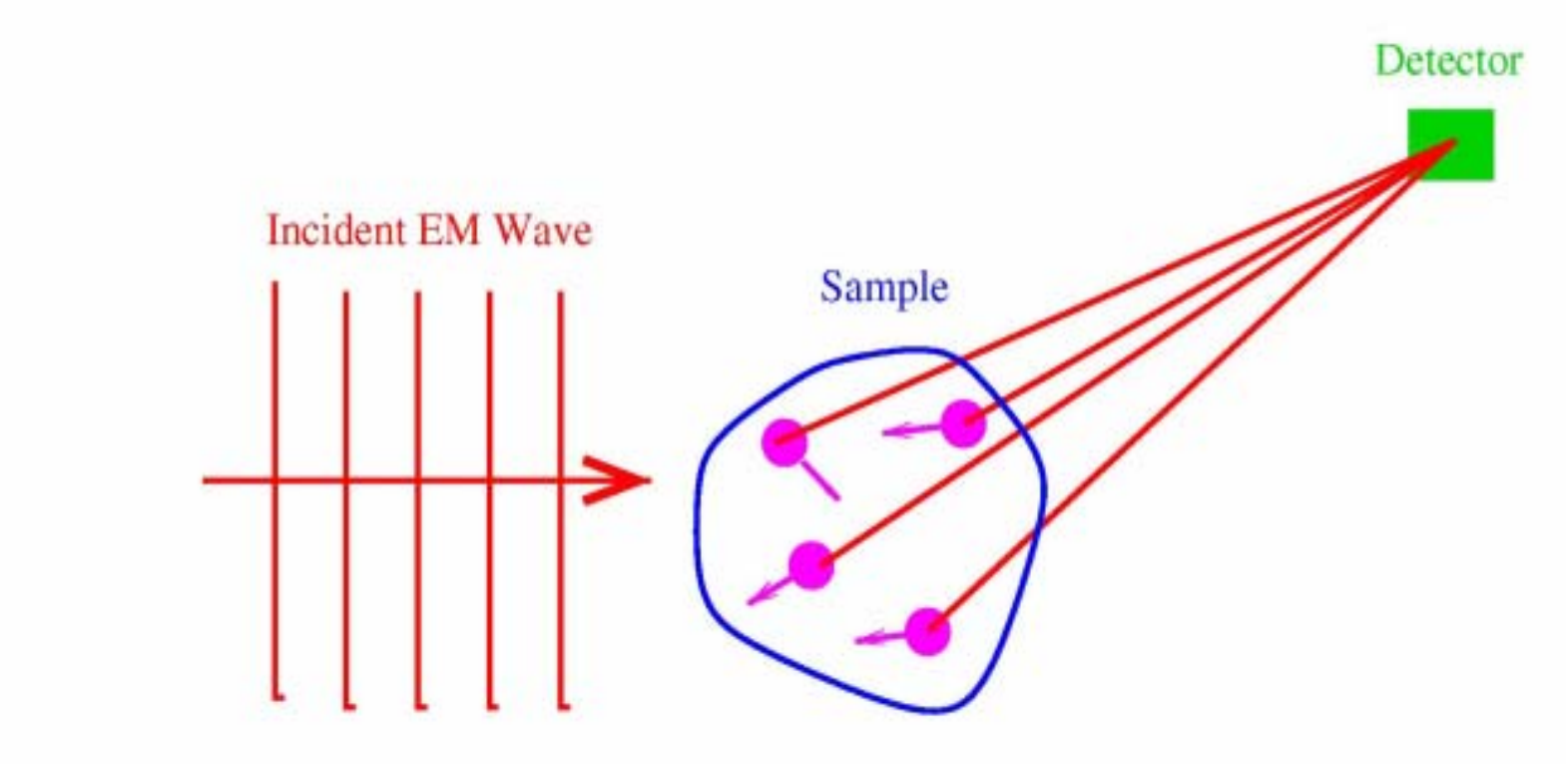


This is just an estimate and exact numbers require integrals over the sample volume and electric field spatial correlation function. Note also, that for small angles, the scattering volume is much smaller than the sample volume.

What to do with coherent x-rays?

- Try to invert the speckle to get information about the exact structure factor. (e.g I. K. Robinson et. al., PRL, 87, 195505)
- Ignore the details of the exact structure factor, but use the time fluctuations of the pattern to study dynamics of the material (XPCS)

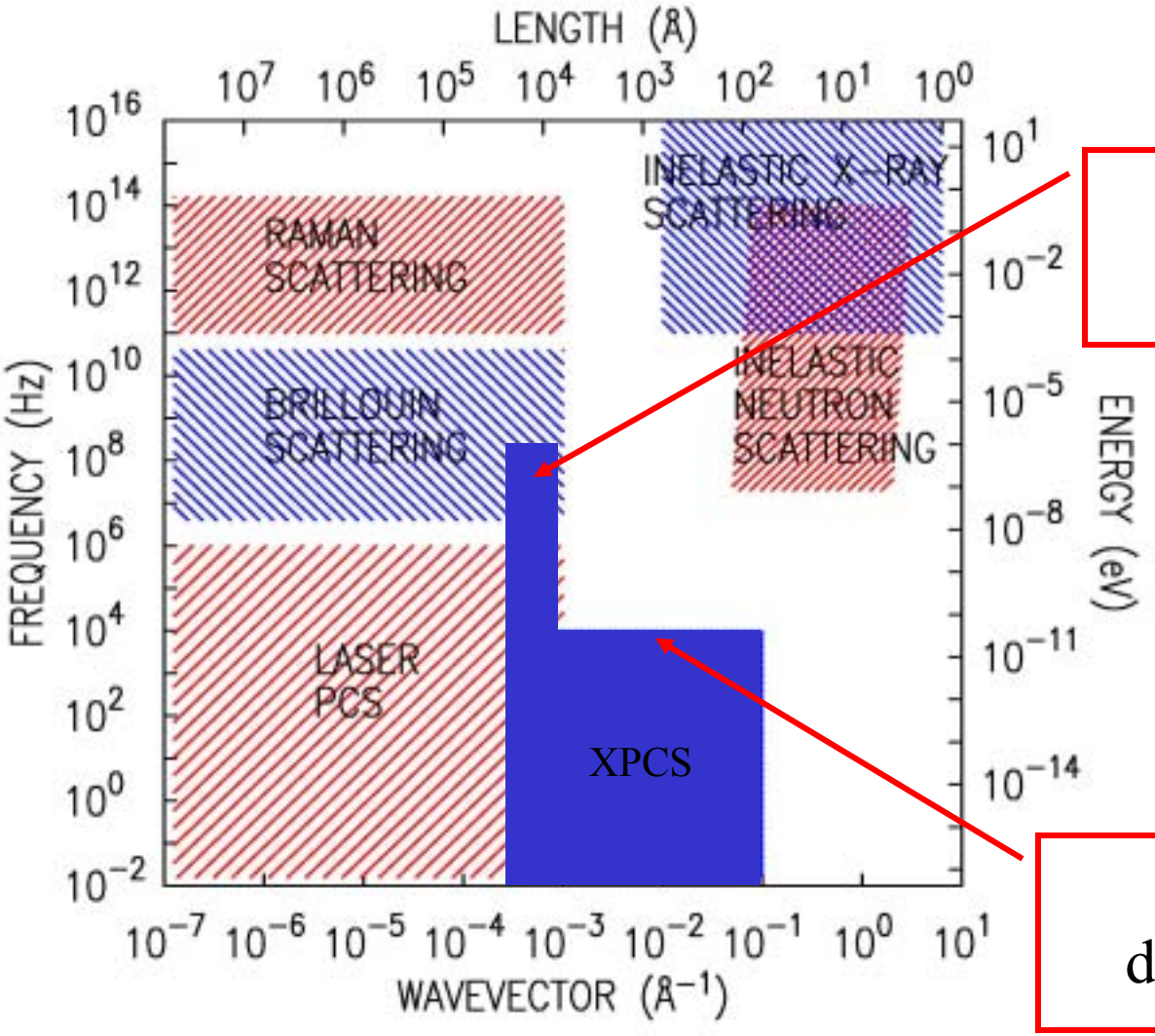
Measuring Dynamics



Typical applications are where the average structure is constant, but the local structure fluctuates.

- Diffusion of particles in solution
- Concentration fluctuations in binary liquids
- Fluctuations of order parameter in a crystal
- Thermally driven surface height fluctuations in a viscous fluid
- Vibration of a membrane

Phase space for XPCS



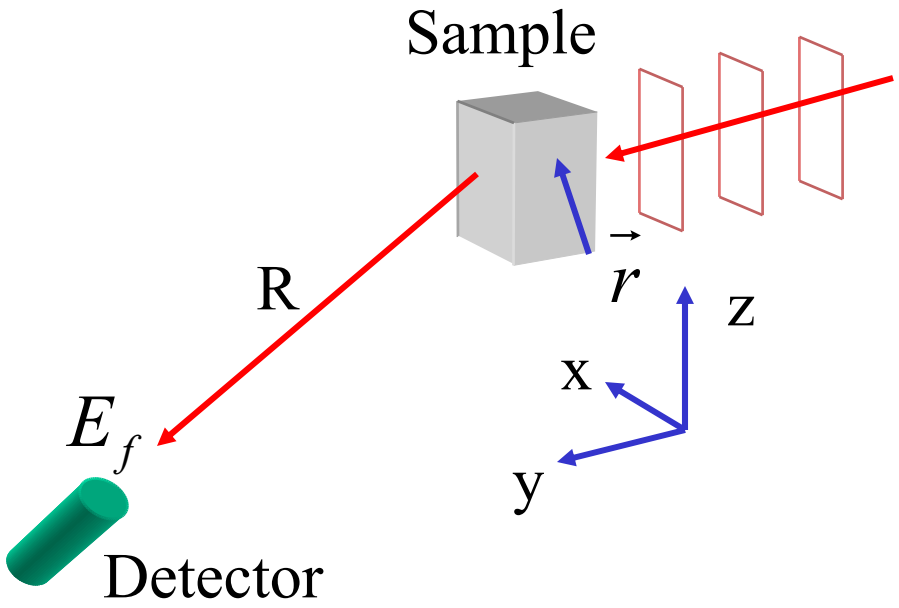
Point detector

CCD detector

Why XPCS rather than PCS?

- Can measure smaller length scales
- Can measure structures associated with crystalline or semi-crystalline order
- Can measure opaque samples
- Multiple scattering not a serious problem
- Stray scattering much less of a problem

The Intensity-Intensity Correlation Function



$$g_2(Q,\tau) \equiv \frac{\langle I(Q,t)\, I(Q,t+\tau)\rangle}{\langle I\rangle^2}$$

How to calculate g_2

- Calculate electric field intensity correlation function at the observation point:

$$G_2(Q,\tau)=\text{f}\exp(\text{i}Q\cdot r')<E_f^2(r,t)\,E_f{}^2(r+r',\text{t}+\text{t})>_{\text{r,t}}\text{d}r'$$

- The fourth order correlations in E, can be reduced to pairs of second order correlation functions

- Assume correlation lengths are smaller than sample size, and the scattering can be factored into independent space and time parts.

Final Result

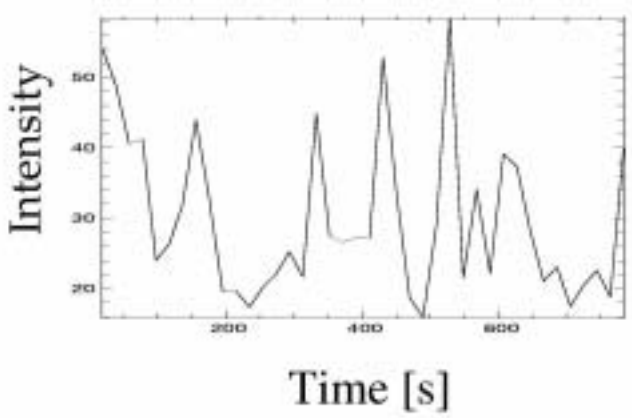
$$G_2(\vec{Q},\tau) = \langle I \rangle^2 \left[1 + \beta f(Q,\tau)^2 \right]$$

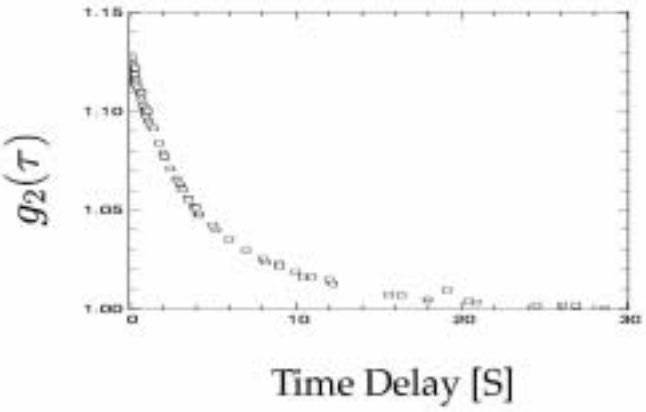
β is a contrast factor related to the beam coherence (varies from 0 to 1)

$$f(\vec{Q},\tau) = S(\vec{Q},\tau) / S(\vec{Q},0)$$

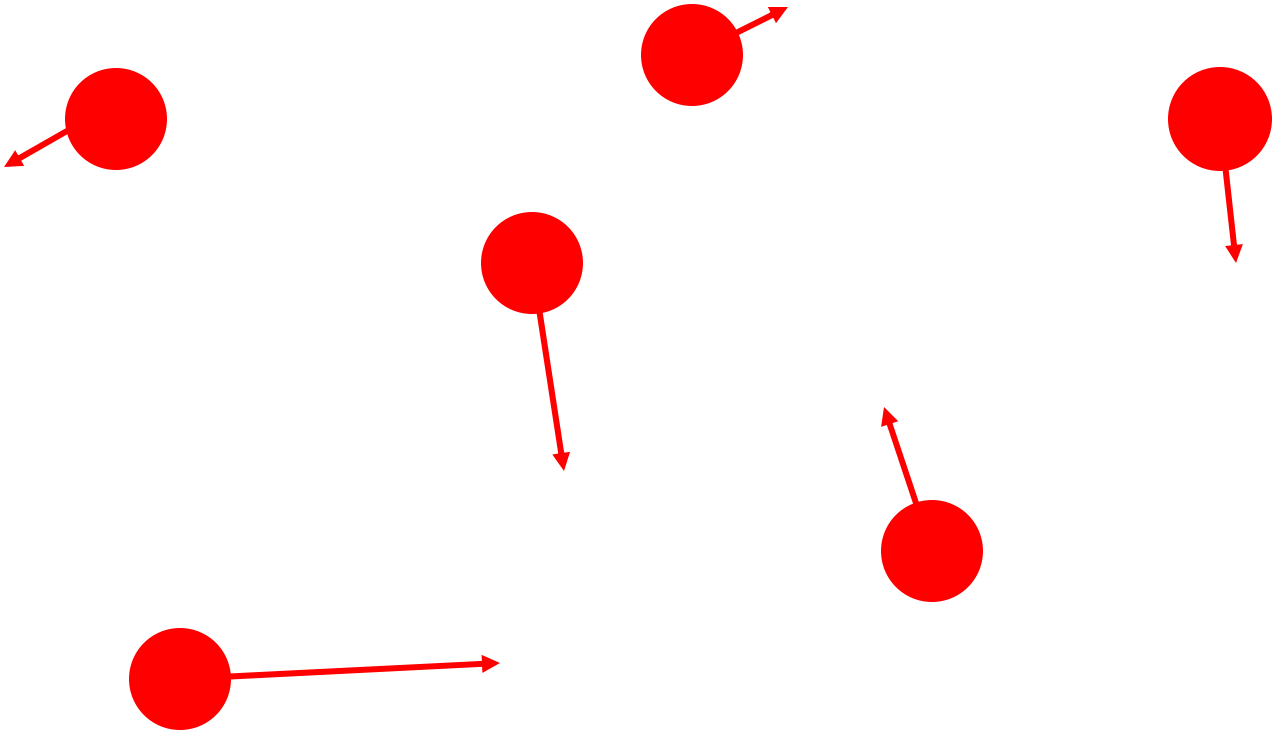
$$S(\vec{Q},\tau) = \left\langle \int e^{i\vec{Q}\cdot\vec{r}} \rho_e(0,0)\, \rho_e\left(\vec{r},\tau\right) d\vec{r} \right\rangle$$

Intensity – intensity correlation function yields the dynamic structure factor of the material


Intensity
50
40
30
20
200
400
600
Time [s]


$g_2(\tau)$
1.15
1.10
1.05
1.00
0
10
20
30
Time Delay [S]

A dilute colloidal suspension



Dynamics Structure Factor for Brownian Motion

$$f(Q,\tau) = \exp(-DQ^2\tau) = \exp(-\Gamma\tau)$$

Stokes Einstein Relation

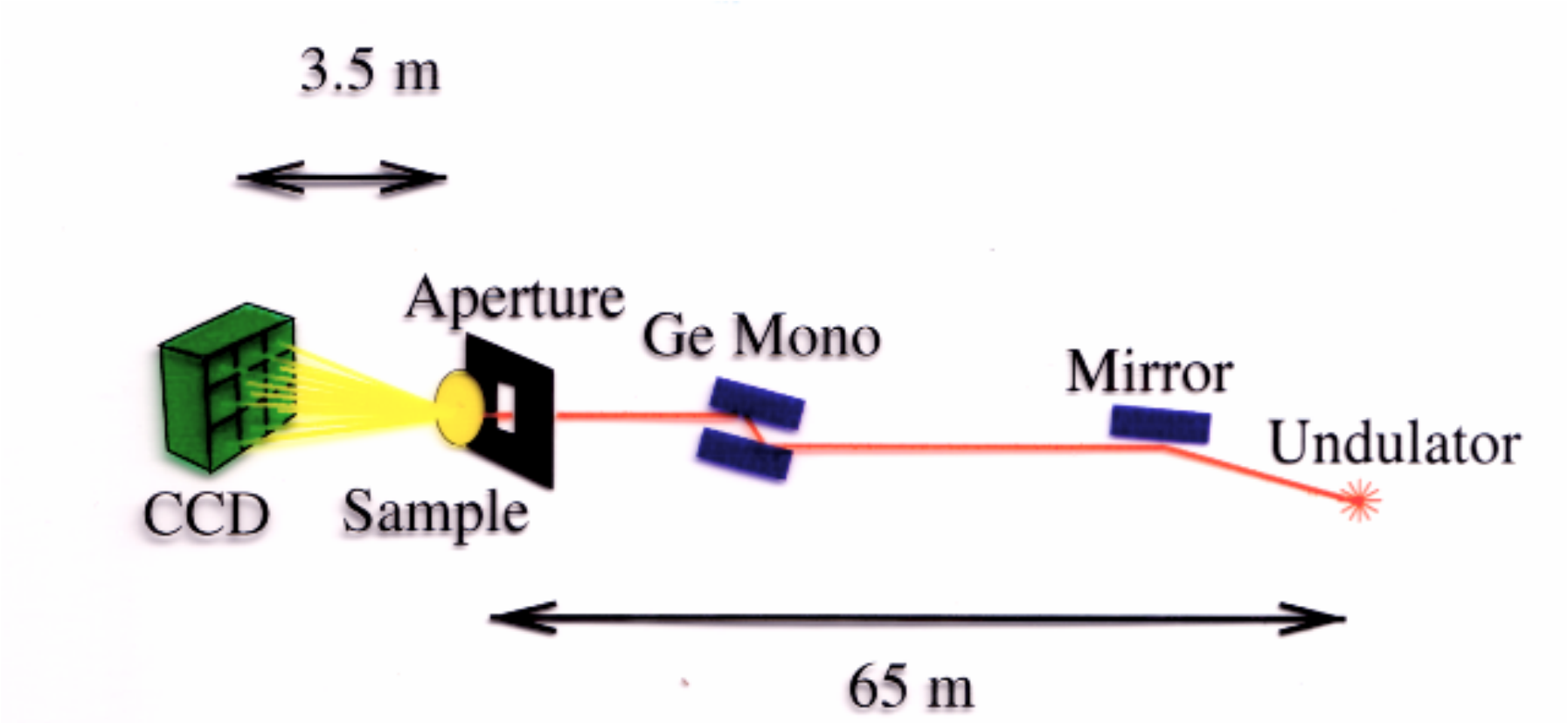
$$\Gamma = DQ^2 = k_B T Q^2 / 6\pi\eta a$$

a → particle size

η → viscosity

T → temperature

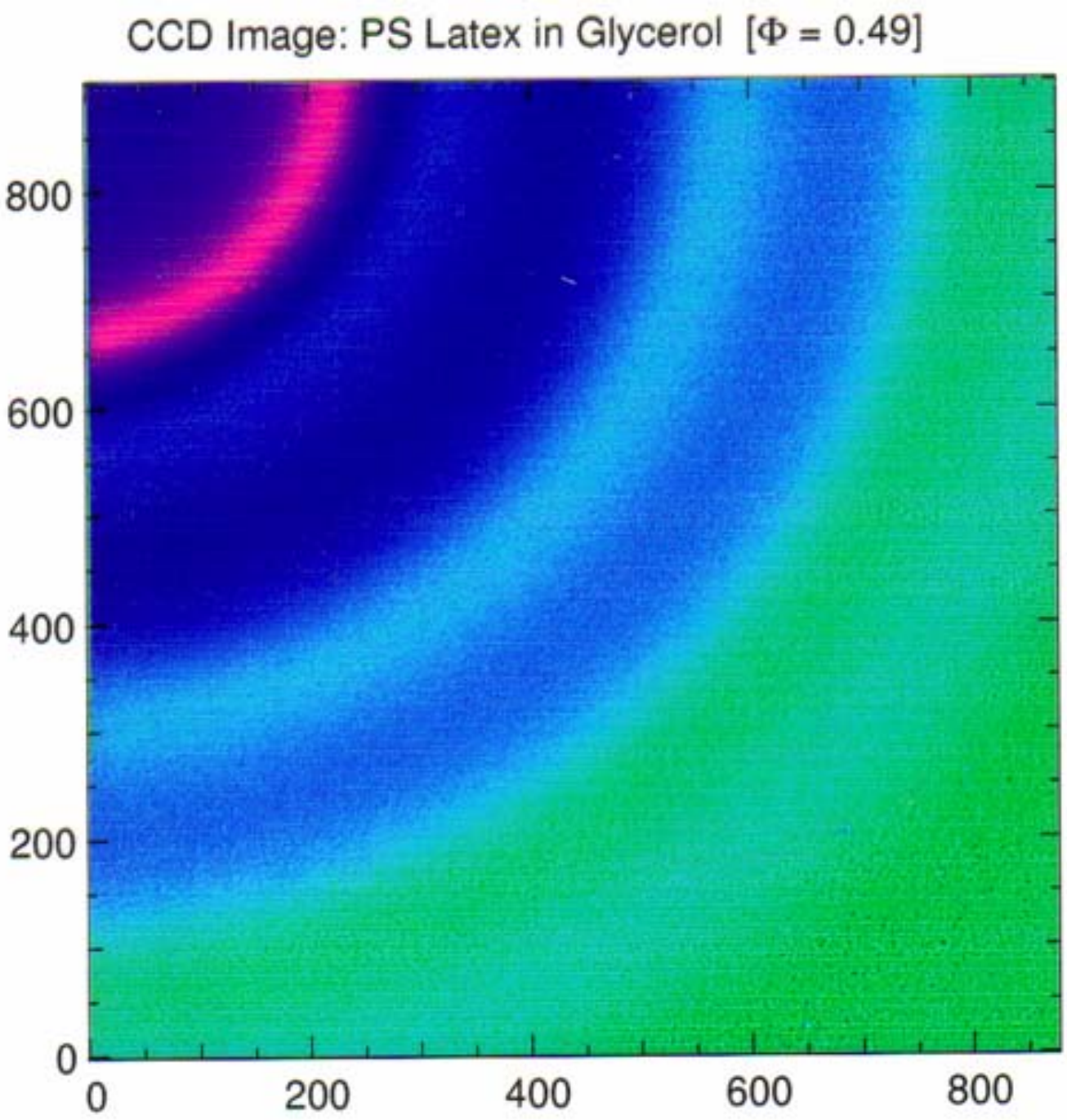
Setup for XPCS at Sector 8 of the APS



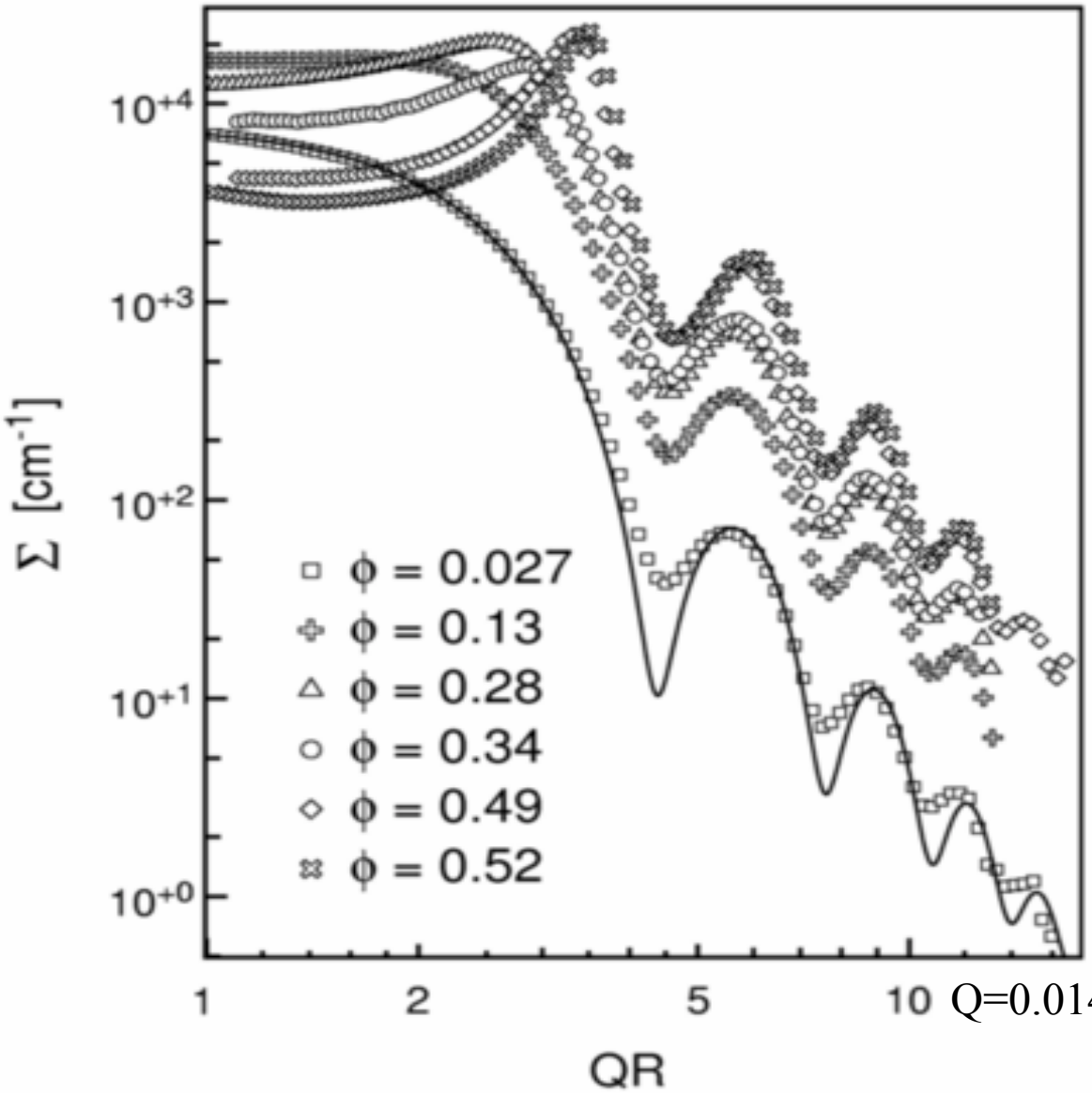
Dynamics of Colloidal Diffusion

L. B. Lurio, D. Lumma, A. R. Sandy, M. A. Borthwick, P. Falus, and S. G. J. Mochrie J. F. Pelletier and M. Sutton Lynne Regan A. Malik and G. B. Stephenson PRL 84, 785 (2000)

- Charge stabilized suspension of polystyrene latex in glycerol
- 67 nm radius particles
- Volume fractions ranging from 2% to 57%
- Technological Relevance
  - Paints, Inks, Foods, Cosmetics
  - Protein crystallization
  - Self assembled nano-structures

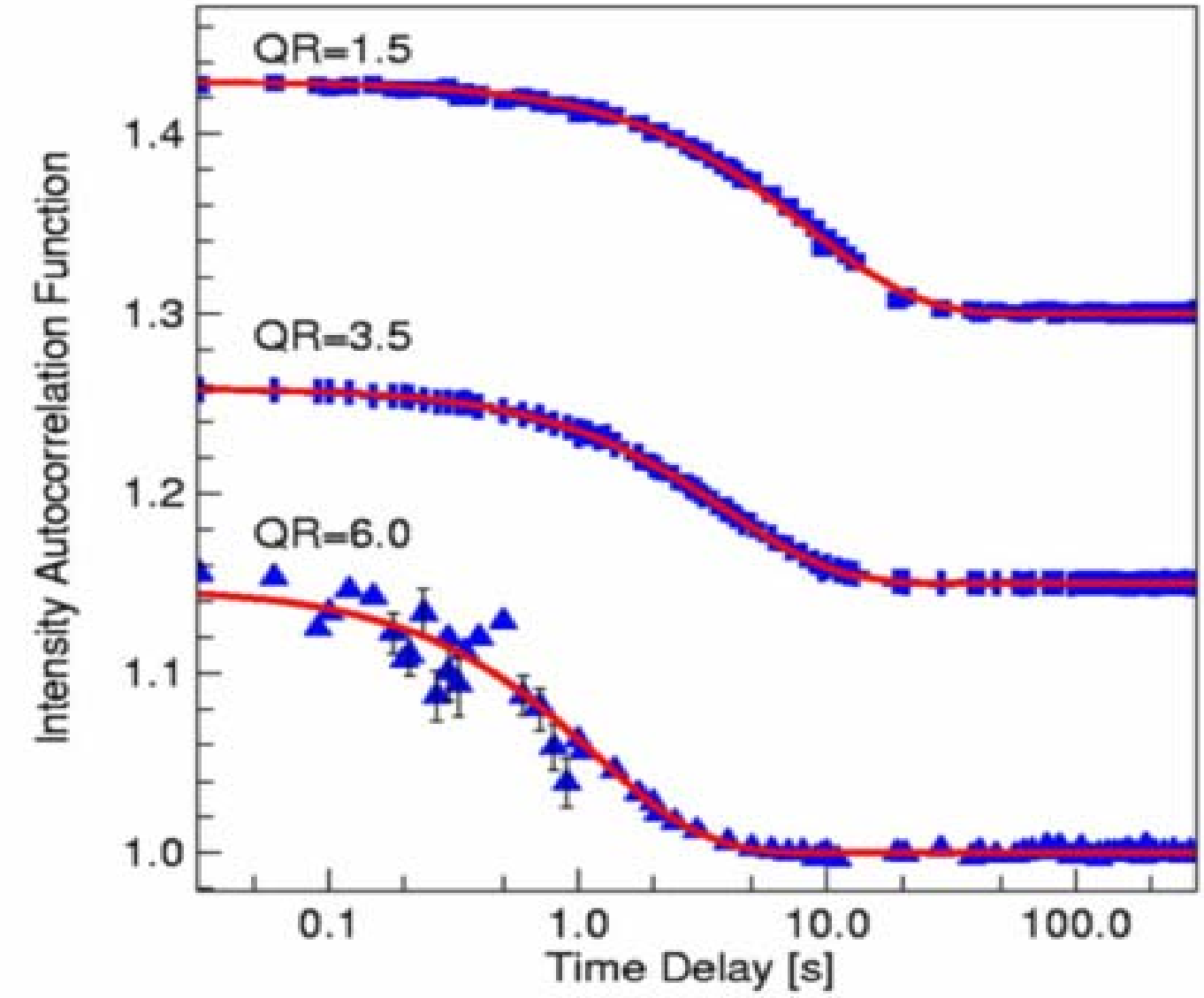

CCD Image: PS Latex in Glycerol [Φ = 0.49]
800
600
400
200
0
0
200
400
600
800

Static Structure



Q=0.014 Å^{-1}

Dynamics


QR=1.5
QR=3.5
QR=6.0
Intensity Autocorrelation Function
1.4
1.3
1.2
1.1
1.0
0.1
1.0
10.0
100.0
Time Delay [s]

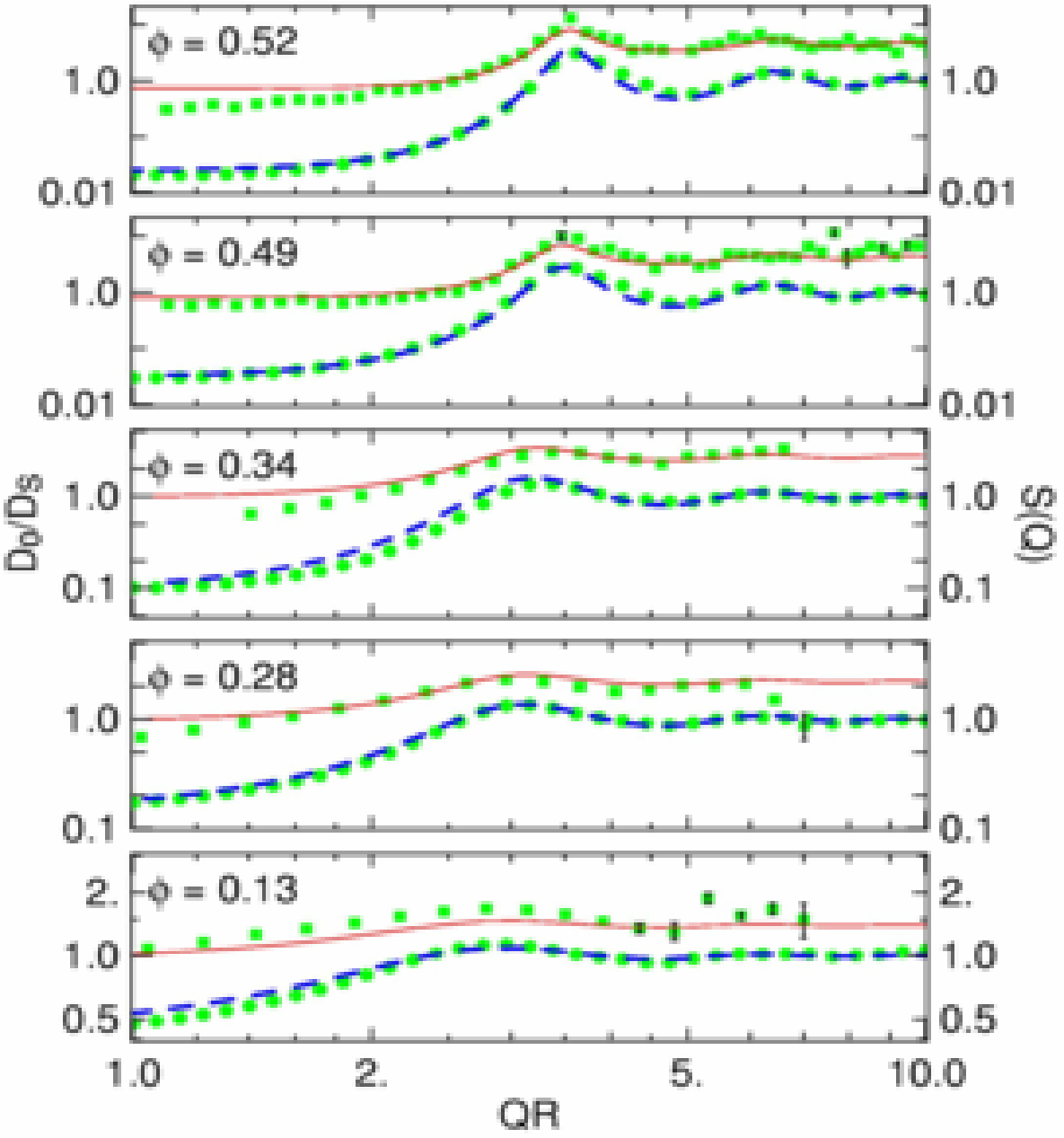
What about concentrated suspensions?

Two modifications to Brownian dynamics

1. Structural correlations lead to a slowing down of dynamics
2. Hydrodynamic interactions further modify the dynamics at high concentration
3. These effects can be calculated for the initial decay rate of the correlation function, but the f(Q,t) will not generally be an exponential at long times.

$$D(Q) = D_0 H(Q) / S(Q)$$

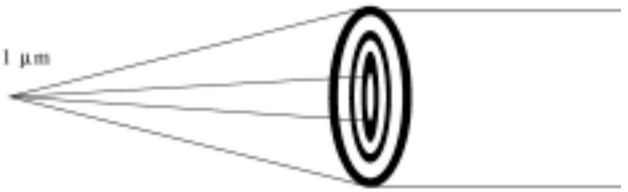
Short Time Diffusion Constants



Example 2: Equilibrium atomic fluctuations in Fe3Al

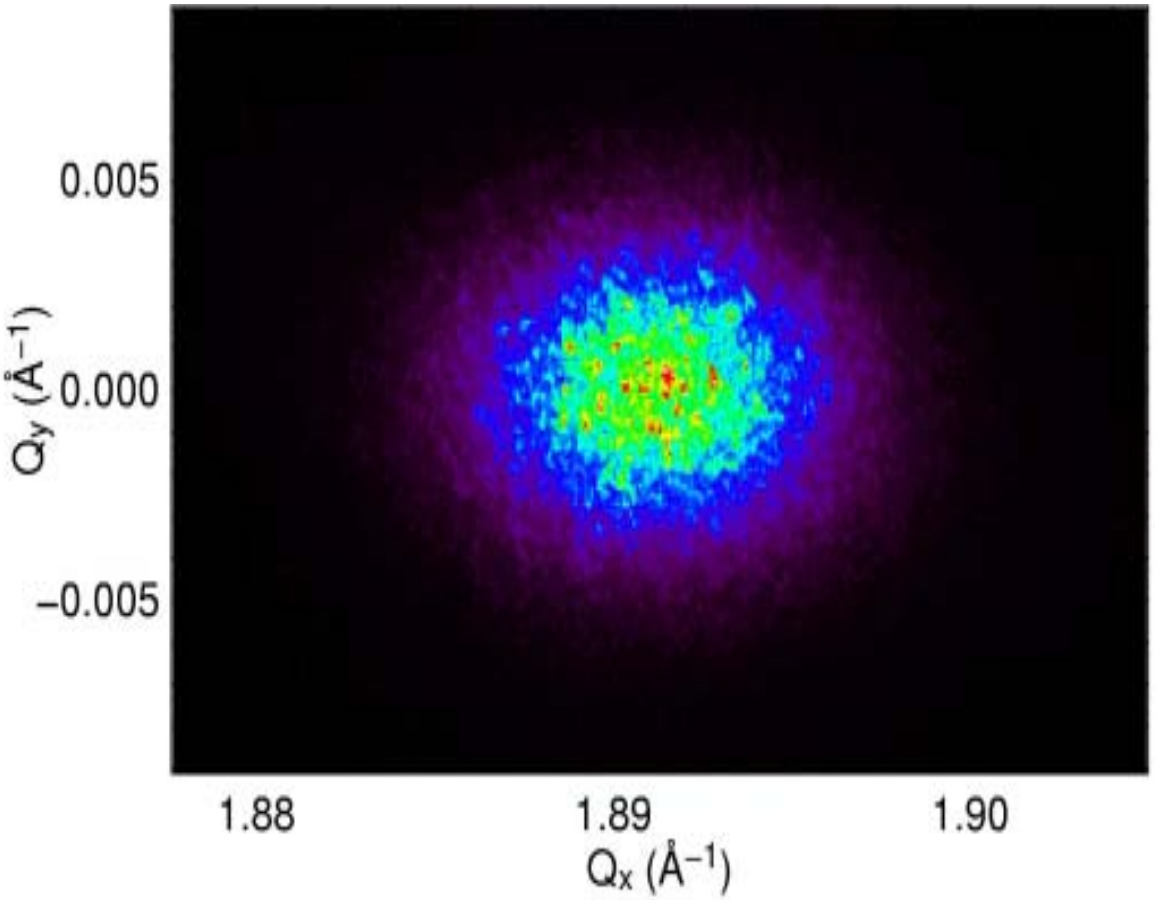
Khalid. Laaziri, M. Sutton, *et al*.

- Look at scattering about a Bragg peak rather than small angle scattering
- Longitudinal coherence length is now important
- Two relevant length scales
- Use of Focusing Optics

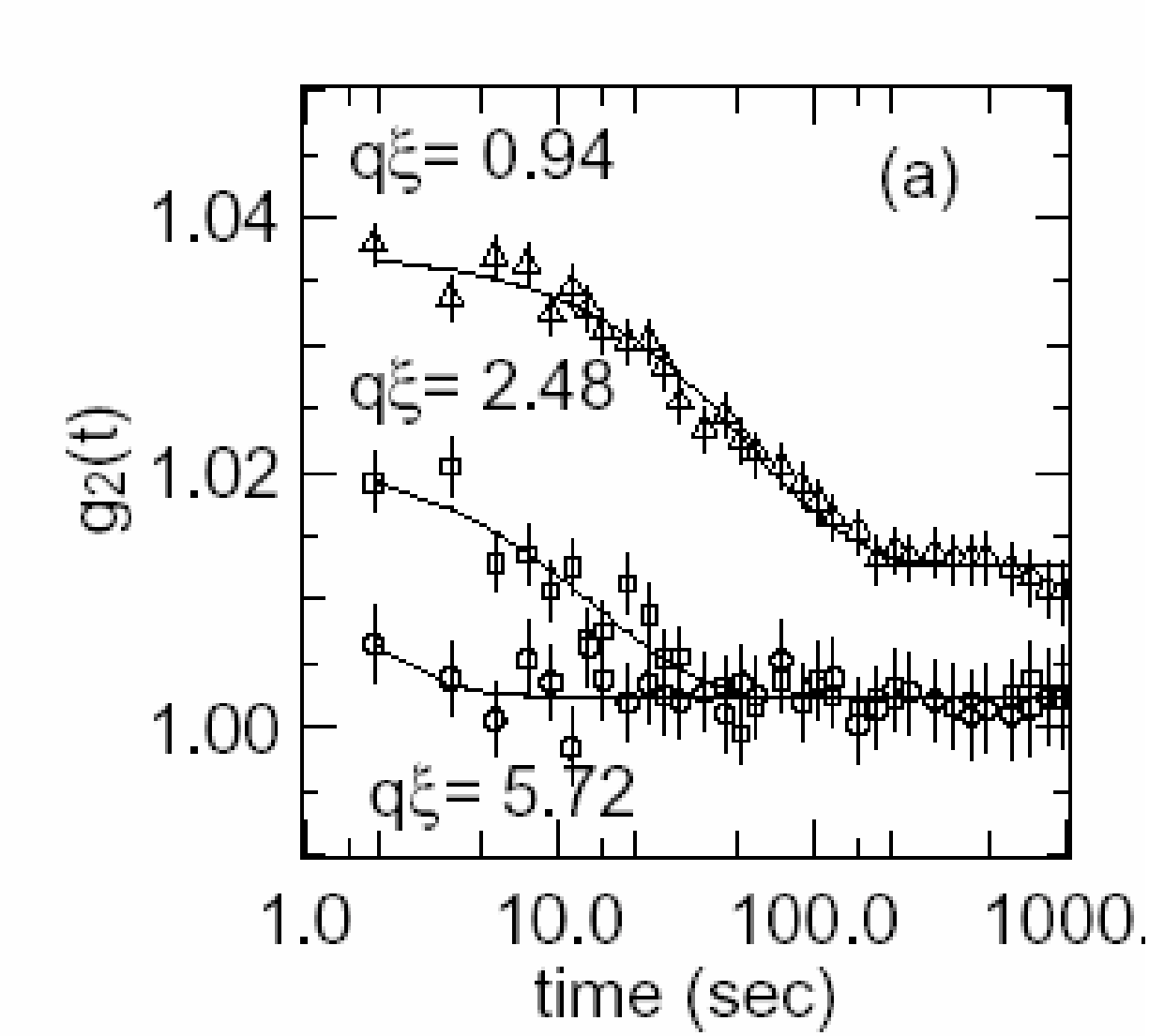


Fresnel Zone Plate

Scattering around the Fe_3Al (1/2,1/2,1/2) superlattice peak at 555C



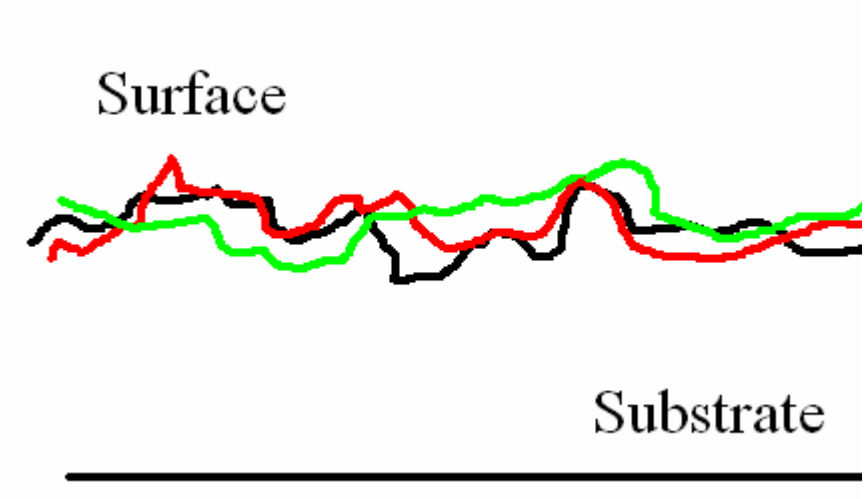
Results



Dynamics in Polystyrene Films

Hyunjung Kim, A. Ruhm, L. B. Lurio et al., Physical Review Letters **90** (6), 068301 (2003).

- Surface height fluctuations in PS films driven by thermal energy
- Surface configuration diffuses from one random configuration to another
- XPCS measures relaxation time vs. length scale



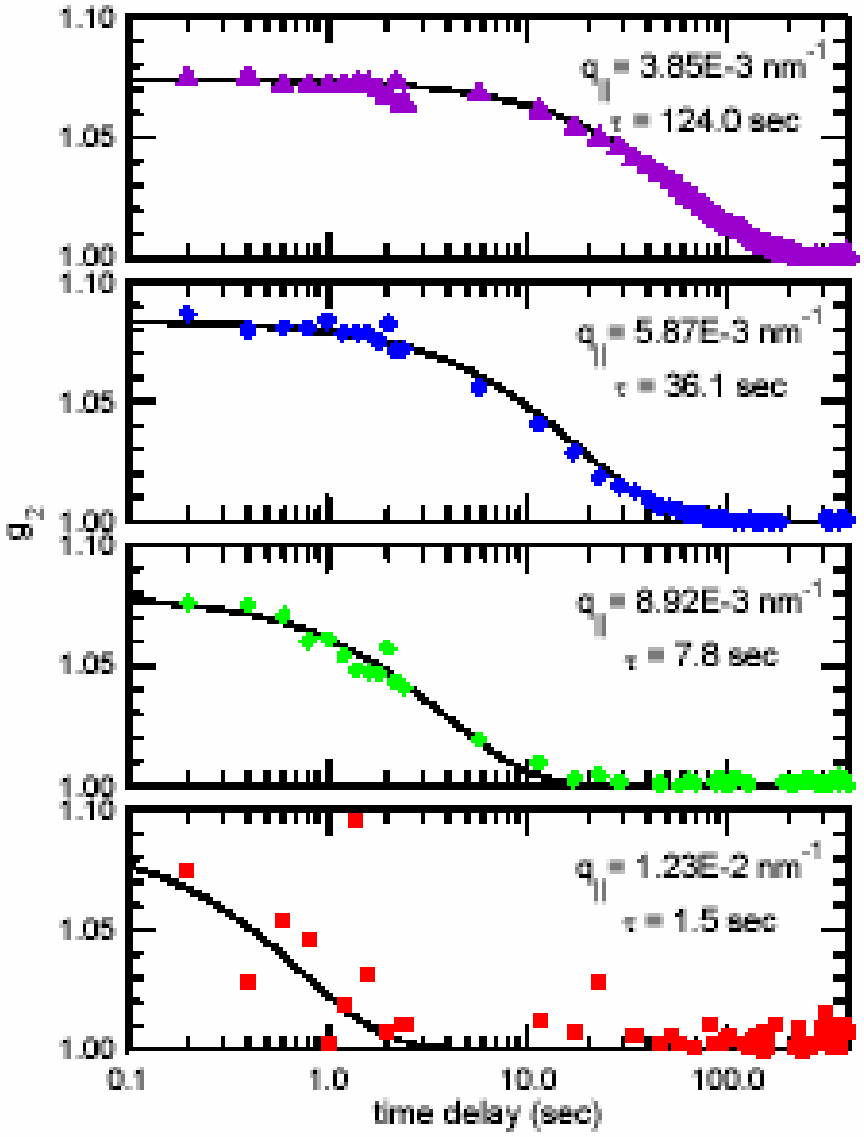
What do you learn

- Relaxation time as a function of in-plane wavelength measures the ratio of viscosity to surface tension
- Surface displacement is due to motion throughout film.

Time Correlation Functions

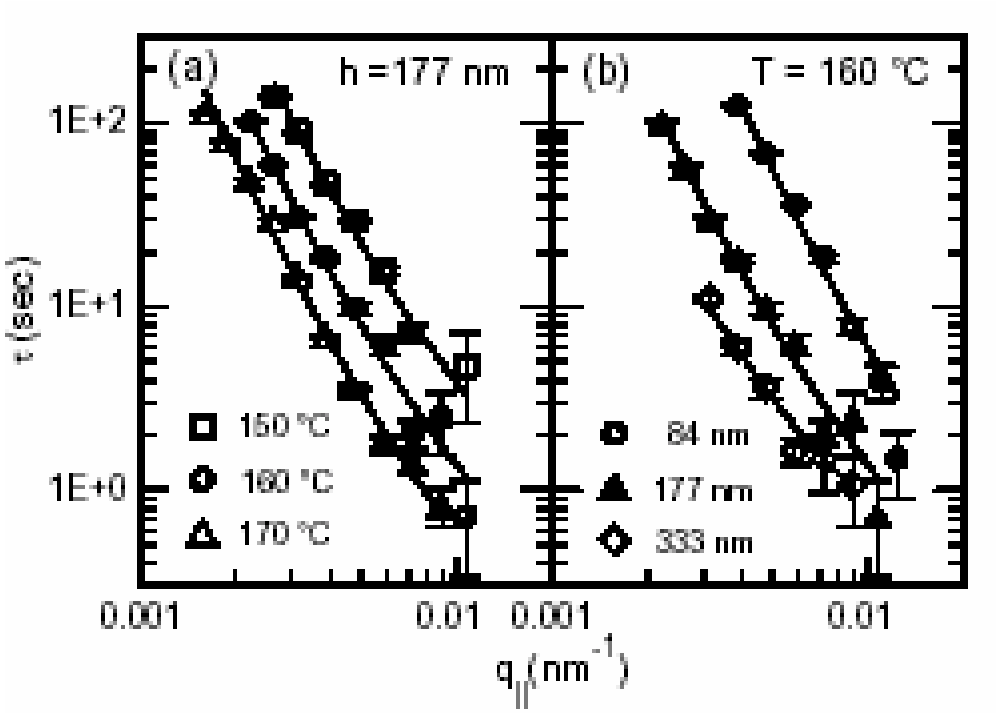
$$g_2(\tau) = \frac{\langle I(t)I(t+\tau)\rangle_t}{\langle I\rangle^2}$$

$$\tau = \frac{2\eta\left[\cosh^2(qh) + q^2h^2\right]}{\gamma q\left[\sinh(qh)\cosh(qh) - qh\right]}$$



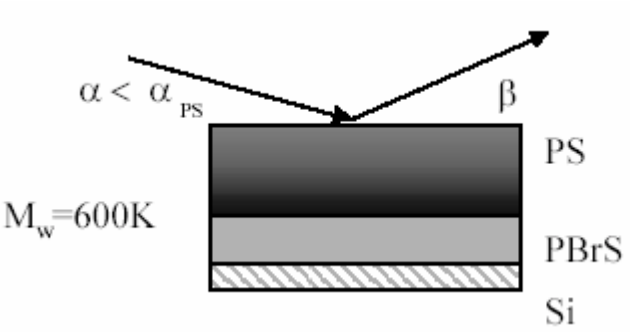
Depth and wavelength dependence agree with theory

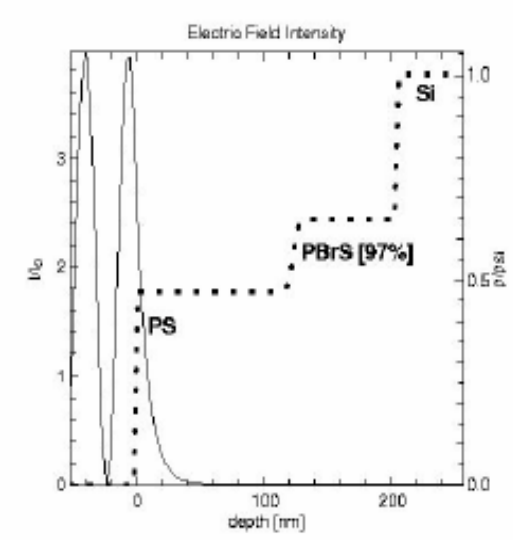
(Choose viscosity as independent parameter, within a factor of 2)

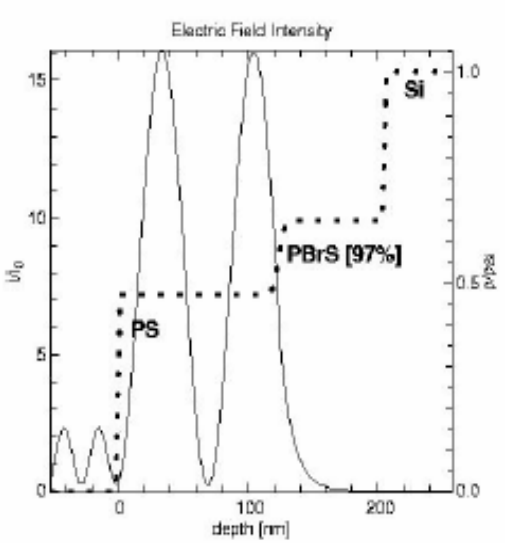


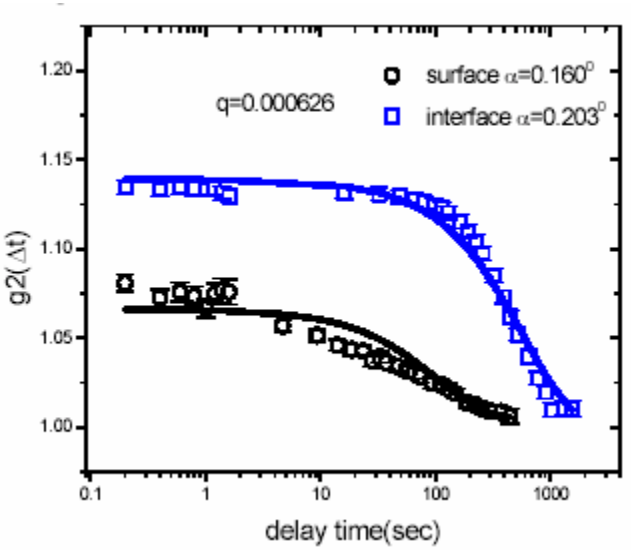
What about Multilayer Films?

- PS-PBrS Bilayers: X. Hu, X. Jiao, S. Narayanan, L. Lurio and J. Lal









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- **This talk:** http://www.imm.aps.anl.gov
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- **Dynamic Light Scattering:** B. Berne and R. Pecora, "Dynamic Light Scattering", Dover, 2000.
- **Coherence:** J. Goodman, "Statistical Optics", Wiley, 1985.

Some References

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- 2 S. B. Dierker, R. Pindak, R. M. Fleming et al., Physical Review Letters **75**, 449 (1995).
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- 11 D. Lumma, L. B. Lurio, S. G. J. Mochrie et al., Reviews of Scientific Instruments **71** (9), 3274 (2000).